Physical Properties of Actinde and Rare Earth Compounds
JJAP Series 8 (1993), pp. 15–19

Purification of Uranium Metal

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(Received June 30, 1992)

We developed the system for purifying uranium metal and its metallic compounds and for growing highly pure uranium compounds to study their intrinsic physical properties. Uranium metal was zone refined under low contamination conditions as far as possible. The degree of the purity of uranium metal was examined by the conventional electrical resistivity measurement and by the chemical analysis using the inductive coupled plasma emission spectrometry (ICP). The results show that some metallic impurities evaporated by the r.f. heating and other usual metallic impurities moved to the end of a rod with a molten zone. Therefore, we conclude that the zone refining technique is much effective to the removal of metallic impurities and we obtained high purified uranium metal of 99.99% up with regarding to metallic impurities. The maximum residual resistivity ratio, the r.r.r., so far obtained was about 17–20. Using the purified uranium, we are attempting to grow a highly pure uranium-titanium single crystals.

KEYWORDS: uranium, zone refining, purification, crystal growth, ICP

§1. Introduction

It would be no exaggeration to say that our major concern for materials developments has been focussed on the reduction of oxide ores and on the deoxidization and the purification of reduced metals, in the long history of human beings. The advance of our technologies in the courss of our history has enabled us to handle more active metals, which had been difficult to reduce and purify. Among a variety of elements, the rare earths and the actinides are the most active elements. So, we could have obtained relatively highly pure metals of these elements only recently.[1)]

Recently, the actinide elements and their compounds are attracting much attention of many researchers. Major attention on one side arises from the nuclear fuel technology.[2)] That is the treatment of nuclear wastes whose main problem is evoked by the actinide elements contained in them. Several solutions are proposed such as their recycling in the nuclear fuel, their annihilation through some nuclear reactions and lastly their utilization by the creation of new useful materials using them. As the actinide elements are the last elements left for the human beings, the last solution may give us a possibility to realize one of our dream, namely, synthesizing new innovative materials. Another attention on other side arises from a basic theory of the solid state physics in connection with the so-called *f*-electrons. It is anticipated much that the *f*-electrons behave very uniquely and give us the key to understand the electron states in solids, which is the major research field of the solid state physics. In these sense, the research of the actinide compounds is very important.[3)]

To advance in the research fields mentioned above, we need target materials of high quality. Even small amounts of impurities in them would conceal their intrinsic properties. Uranium and its compounds are considered to be the entrance to study of actinide elements, because of its large available quantity and its very weak toxicity and radio activity compared to other actinide elements. Therefore, we initiated our study by purifying the uranium metal and then contemplate growing single crystals of its compounds of high quality, using the highly purified uranium metal.

As mentioned above, the purification of uranium is very difficult to carry out. The uranium is chemically very active and its affinity with interstitially gaseous atoms is very strong. What is worse for the uranium is that the vapor pressure ratio between its oxide and the metal is low. This means that the melting in a high vacuum would not result in the deoxidization, that is usually the case in the chemically active metals such as the IVa, the Va, and the VIa transition metals, such as hafnium, tantalum and molybdenum, and the rare earth metals such as yttrium.[1)] The thorium also has a large value of this ratio, about 10^3, and could be deoxidized by melting it in a high vacuum.[1)]

The conventionally industrial reduction and purification system for the uranium is composed of the chemical purification, reduction of oxide with calciium or iodide, and the molten salt electrolysis.[4)] However, the purity of the uranium obtained by these conventional processes would not satisfy the demands evoked by the research activities in the new materials development and the solid state physics. Here, we adopted the two step purification processes to purify the conventinally pure uranium further, both of which are proven to be effective to purify the active metals. One is the zone refining and the other is the electro-transport, or the solid-state electrolysis.[5,6)]

The purification process, however, should be carried out in a qualified environment to get rid of picking up impurities during the process. Here, we developed the system for the purification process, which realized a reasonablly high vacuum and the environments compatible with the heated or melted uranium. In this section, we will describe the detail of the developed purification system and the procedures of the actual purification. We will also show the results of purification of uranium, which were examined by the electrical resistivity measurement and by the chemical analysis.

§2. Experimental

2.1 *Development of instruments*

The uranium is chemically very active and easy to oxidize even in a high vacuum. Figure 1 shows the standard free energy, ΔG for the formation of its dioxide, UO_2.[7-9] The oxygen partial pressure, P_o, equilibrating to UO_2 at about 1400 K is estimated to be from 10^{-30} to 10^{-34} atm. In the meantime, the reported equilibrium oxygen dissociation pressure, P_{vo} is about 10^{-8} atm at 1400 K, although it depends strongly on the x in UO_{2+x}. These mentioned above indicate that the high degree of vacuum is needed to get rid of picking up oxygen in the course of the uranium treatment. However, the available technology could not realize such a high vacuum at present.

Figure 2 shows the reported vapor pressure of the uranium metal and the uranium dioxide, UO_2.[8,9] The vapor pressure of the uranium metal at its melting point is 1.2×10^{-11} atm, namely, 1.5×10^{-7} Pa. The reported vapor pressure of the UO_2 at 1300 K is about the same as shown in Fig. 2. Therefore, the realistic target of the vacuum will be that better than 10^{-7} Pa. We set our target of the vacuum of our apparatuses to be better than 10^{-9} Pa as a base pressure and to be better than 10^{-8} Pa as a working pressure.

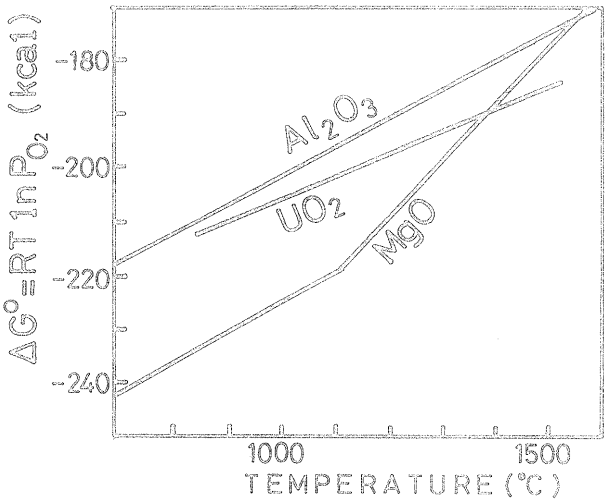

Fig. 1. Standard free energies for formation of UO_2, Al_2O_3 and MgO.

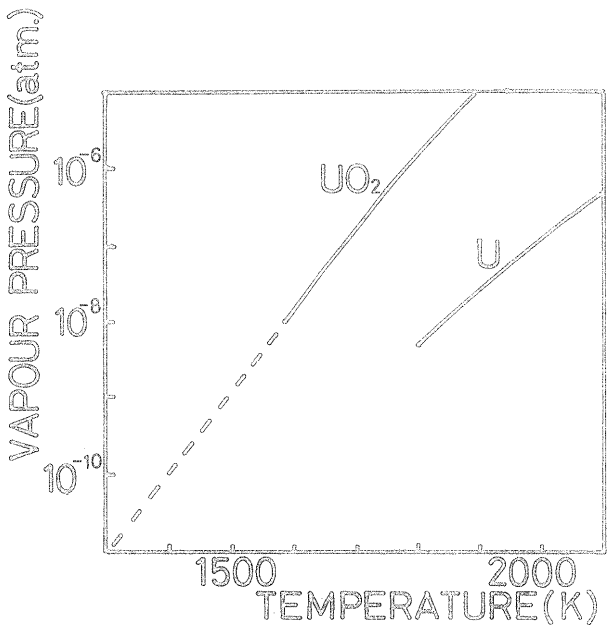

Fig. 2. Vapor pressures of UO_2 and uranium metal.

Figure 1 also shows that alumina and magnesia crucibles are not suitable for the uranium-melting. Looking into the phase diagrams, it is found that the molten uranium is almost incompatible with any metals and refractory compounds. The experiences accumulated up to now suggest that the only water-cooled copper hearth is compatible with the molten uranium. Thus, the floating zone technique or the adoption of the water-cooled copper hearth is the only choice for the zone refining. However, the self-sustainability of the melted part of uranium was uncertain and the drop-off of the melted uranium will cause serious problems. So, we adopted the water-cooled copper hearth.

About the heat source, there are several choices, each of which has its advantages and disadvantages. The possibility of contamination with the tungsten makes us discard the electron beam melting. Also, the optical heating system appears difficult to stand together with the high vacuum system at present. For these reasons, we decided that the r.f. heating system would be the best choice at present.

Figures 3 and 4 depict the schema of the developed r.f. heating zone refining apparatus and the electrotransport instrument. Table I shows the major features of these instruments. A special copper-made hearth was developed to enable the r.f.-power to enter the uranium metal effectively through the electrically-conductive copper hearth. The developed hearth is completely compatible with the required high vacuum.

2.2 *Purification of uranium*

The uranium metal whose content of impurities is shown in Table II were zone refined several times in a high vacuum or in a highly pure helium environment. In

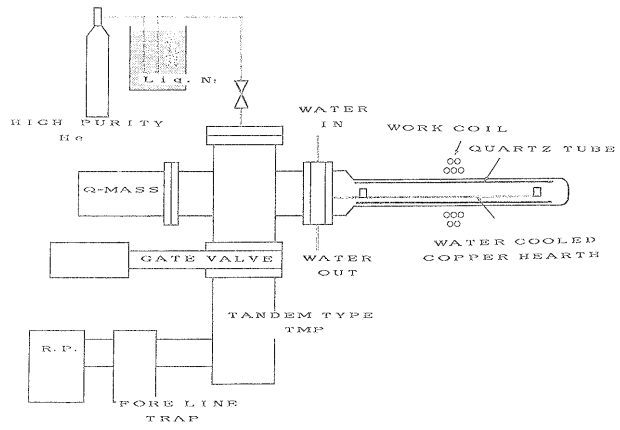

Fig. 3. Schematic illustration of the r.f. heating zone refining apparatus.

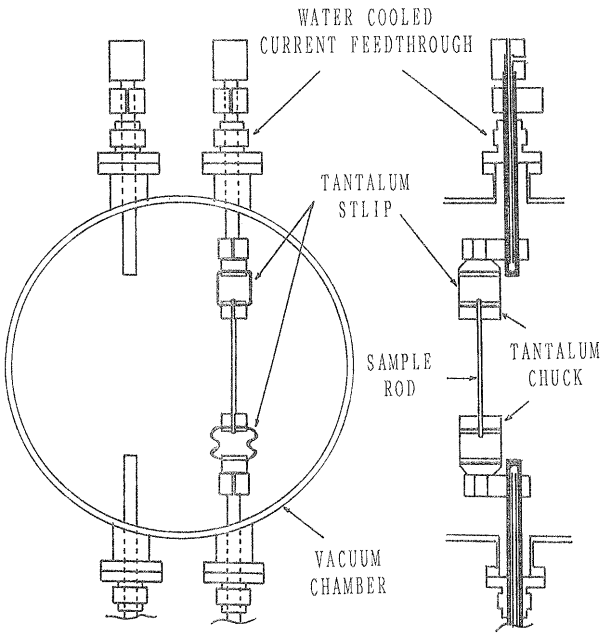

Fig. 4. Schematic illustration of the high vacuum electrotransport apparatus.

Table I. Features of developed apparatuses.

	S.S.E.		Horizontal zone refining
Vacuum system	•Ion pump •Ti sublimation pump with Liq. N_2 shroud. •Turbo molecular pump.	Vacuum system	Tandem type turbo molecular pump.
Base pressure	$\sim 4\times10^{-9}$ Pa	Base pressure	$\sim 7\times10^{-9}$ Pa
Current		Output power	15 kW
Voltage	DC 0 A ~ 1000 A	Frequency	400 kHz
Sample length	DC 0 V ~ 6 V 120 mm max.	Sample length	200 mm max.
		Width of molten zone	~ 15 mm

Table II. Impurity content in starting uranium (ppm).

Al	15	C	50	Fe	50	Nb	25	Ti	25
Ag	25	Ca	25	Mg	50	Ni	50	V	25
B	25	Cd	25	Mn	25	Pb	50	W	25
Be	25	Cr	25	Mo	25	Bi	50	Zn	25
Bi	25	Cu	25	Na	25	Bn	25	Zr	50

the course of the experiment, it was found that the molten part of the uranium became thermally unstable due to the interaction with the water-cooled copper hearth and due to the complicated interaction with the r.f.-power supply. The introduction of helium into the system stabilized the molten-part of the uranium substantially.

Also, it was found that the pretreatment of uranium metals and sequentially proper treatment of uranium metals during the zone refining were important for the success of the zone refining.

The uranium metal was purified as follows;

A. Melting in an ultra high vacuum.
B. Zone refining of several times in an ultra high vacuum.
C. Zone refining of several times in a helium gas environment of one atmosphere.
D. Cutting down end side of 1/3 of uranium rod.
E. Zone refining of several times in an ultra high vacuum.
F. Zone refining of several times in helium gas atmosphere.
G. Annealing.

The purified part of the uranium metal was then solid state electrolysized in the electrotransport instrument for about one week just below the melting point.

2.3 *Analysis of purity*

We measured the electrical conductivity of the purified uranium in the temperature range of 4.2 K–300 K. The degree of purity of the uranium was primarily judged by the so-called r.r.r. (residual resistivity ratio), the resistivity ratio between at 300 K and at 4.2 K. The chemical analysis was carried out by the ICP, inductive coupled plasma emission spectroscopy, technique.[10] As the ICP is not suitable for analysis of gaseous elements such as hydrogen, nitrogen, oxygen etc., we analyzed the uranium metal purified by only zone refining process which is effective for removal of metallic impurities as said before.

Analyzed parts of the purified uranium are shown in Fig. 5 in the relation with the zone refining process mentioned above. The operating conditions of the ICP are shown in Table III. The uranium metals were solved in a heated nitric acid. The acid concentration was controlled to be 8 M. The standard solution of the analyzed elements was also controlled to have the same nitric acid concentration. Four kinds of the standard solution were prepared, whose concentrations of the analyzed elements are 0, 5, 10 and 15 ppm.

To simplify the analysis, we restricted number of analyzed elements by following conditions.

1. Elements which analysis is difficult for the ICP should be excluded.
2. Elements whose chemical properties are similar each other such as the rare earth elements should be represented by a typical element.

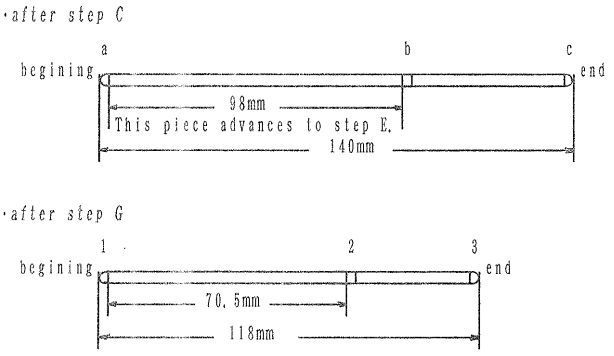

Fig. 5. Analysed parts of the uranium metal rod purified by zone refining.

Table III. Operating conditions of the ICP.

Hitachi dual monochromator-ICP%AES-P%5200	
R.F. power	1 kW
Argon gas flow rate	
Plasma	12 l/min
Nebulizar	0.5 l/min
Auxiliary	0.5 l/min
Observation height above coil	15 mm
Slit width	
Spectrometer 1	30 μm
Spectrometer 2	30 μm
Grating	
Spectrometer 1	3600 grooves/mm
Spectrometer 2	1200 grooves/mm

Table IV. The concentration of impurites in zone refined uranium metal obtained by ICP analysis. The label a, b, c, 1, 2 and 3 correspond to those in Fig. 1.

(w. ppm.)

	Al	Ca	Cr	Cu	Fe	Mn	Ni	Pb	Si	Sn	Zn
a	10	9.1	1.0	3.6	14.4	—	9.2	0.2	21.5	0	0.4
b	10	3.5	2.3	6.7	53.8	0	32.9	—	28.9	1.2	0.4
c	10	4.6	4.2	11.1	188.4	0.2	96.8	0.2	66.7	6.5	0.8
1	8	8.6	0.9	2.2	8.6	—	5.5	—	17.8	0.9	0.2
2	13	6.6	2.0	4.3	47.8	0	28.5	—	26.5	1.8	0.7
3	25	11.2	4.2	7.1	146.2	0	80.3	0.6	70.0	4.6	1.0
Before z.r.	13	4.4	2.3	17.1	53.1	6.9	33.8	9.6	34.3	2.0	2.2

3. Elements whose extraction by the TBP, which will be explained later, are large, should be excluded.

Consequently, we chose the following elements; aluminum, bismuth, calcium, cadmium, cobalt, chromium, copper, iron, lanthanum, lutetium, magnesium, molybdenum, nickel, lead, praseodymium, scandium, silicon, tin, titanium, vanadium, tungsten, and zinc.

The problem in the ICP analysis of the impurities in the uranium is that many emission spectra from the uranium itself conceal those from the impurity elements. So, the uranium was removed by the extraction method using the TBP (Tri-n-butyl Phosphate). At first, the TBP was mixed with a toluene in the ratio of 1 to 1, then its mixture was made to form a preequilibrium state by shaking them with the 8 M nitric acid solution. We extracted the uranium using such the TBP twice. After the extraction, any uranium in the solution can not be detected by neither the ICP nor the GM survey meter. The blank nitric acid solution of 8 M was prepared by the same procedure as the uranium solution.

The use of the TBP causes another problem, that is, the possibility of the extraction of impurity elements. So, we examined the extraction factor of the impurity elements using the standard solution. The analyzed result of impurity was rectified by its factor.

§3. Results and Discussion

The concentration of the impurities in the zone refined uranium metal is shown in Table IV. The result on the uranium before the zone refining is also shown as comparison. The minimum accuracy of the data is thought to be less than 1 ppm. The elements which can not be detected are not shown in Table IV. As deduced from the zone refining of the rare earth metals, metallic impurities usually move to the end edge of a rod with the molten zone by the process of the zone refining. That is attributed to distribution factor of impurities between the solid and the liquid phases being less than an unity. The typical elements are iron and nickel as depicted in Table IV. The elements whose concentration decrease totally by the zone refining, typical one is manganese, is thought to evaporate in the process of the zone refining in an ultra high vacuum. Behavior of copper exhibited the mixture of above two cases.

Thus, the behaviors of almost all the impurities can be explained and the zone refining is confirmed to be effective for purification of the uranium metal as far as the metallic impurities are concerned. However, the behaviors of aluminum and calcium are strange. These two elements increased their concentration after the zone refining. As for the calcium, we guessed that the contamination from the TBP may be the origin of the contamination. Concerning the increase of aluminum concentration, we can not identify its actual cause at present.

Adding up the concentration of the impurities except for calcium and aluminum in the most purified peace (1 in Table IV), we obtained the value of 36.1 wt·ppm. Judging from this value, the total concentration of metallic impurities in the purified uranium is thought to be less than 100 wt·ppm. So we may think that the high purity uranium metal of 99.99 wt.% is obtained. As for the value of the r.r.r., the best we obtained is around 17–20, being comparable with the best value ever reported in the world.

It is interesting to compare the result of chemical analysis with the r.r.r.. Figure 6 is the r.r.r. of the uranium metal rod after the all zone refining processes. As stated before, the r.r.r. is influenced by the many origins. However, the influences except for impurities are thought to be almost the same in every part of the uranium rod. Further, judging from the case of the zone refining of the rare earth metals, gaseous impurities such as oxygen, nitrogen etc. are thought to be hard to remove. So, the r.r.r. is thought to reflect the concentration of metallic impurities. But, as the effects substitutional metallic impurities on the electrical resistivity will be smaller compared to that of interstitial gaseous impurities, the change of the r.r.r. is smaller than that inferred from the decrease of impurities concentration. Anyway, although the situation of the r.r.r. is very complex, its result supports the result of the ICP analysis.

§4. Conclusion

We developed instruments for the purification of the uranium metals. Using the instruments, we carried out the purification of the uranium metal. We performed the chemical analysis of the purified uranium metal using the ICP and by the electrical resistivity measurement. The purity of the uranium is thought to be improved to be 99.99% up. We are now synthesizing the highly pure

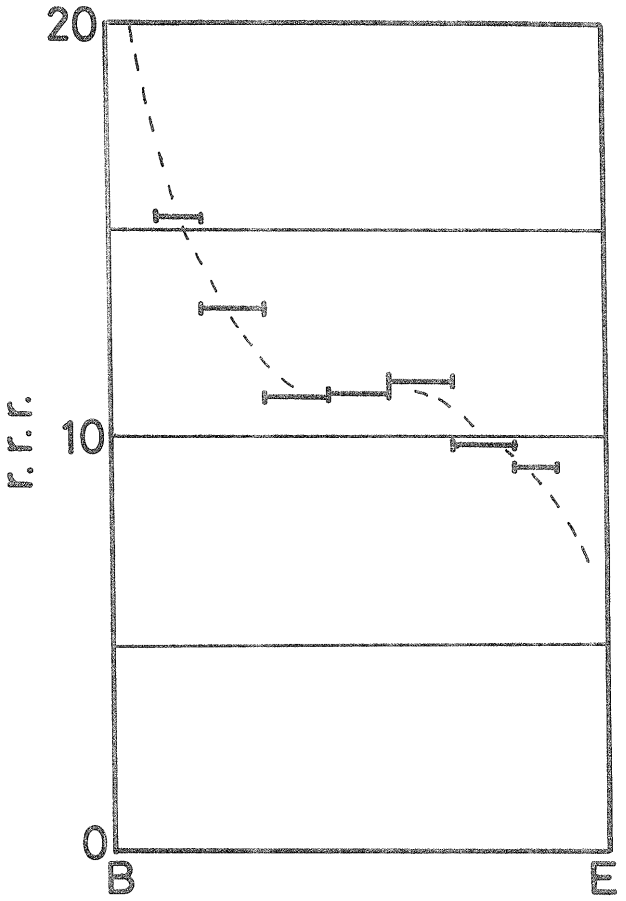

Fig. 6. Residual resistivity ratio (r.r.r.) of the uranium metal rod purified by zone refining.

uranium compounds using the purified uranium.

Acknowledgements

We are grateful for the cooperation of the staff of the Oarai Branch, IMR, particularly Mr. Y. Suzuki, Profs. Y. Shiokawa, and T. Mitsugashira and Prof. H. Kayano, Director of the Oarai Branch. We also thank to Profs. T. Komatsubara, T. Suzuki and T. Kasuya of Tohoku University for their fruitful discussion about zone refining method. We express our sincere gratitude to Prof. I. Sato and Mr. M. Takahashi of IMR for their kind cooperation in the ICP analysis.

This work was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, from 1988 to 1991.

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